

(19) Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) EP 0 984 034 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
08.03.2000 Bulletin 2000/10

(51) Int. Cl.<sup>7</sup>: C08K 5/5419, C08L 23/02

(21) Application number: 99116148.0

(22) Date of filing: 19.08.1999

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 04.09.1998 US 148805

(71) Applicant:  
DOW CORNING CORPORATION  
Midland, Michigan 48686-0994 (US)

(72) Inventors:  
• Feng, Qian Jane  
Midland, Michigan 48640 (US)

- Lee, Kenneth Michael  
Bay City, Michigan 48708 (US)
- Lutz, Michael Andrew  
Hope, Michigan 48628 (US)
- Owen, Michael James  
Midland, Michigan 48640 (US)
- Perz, Susan Victoria  
Essexville, Michigan 48632 (US)
- Suzuki, Toshio  
Midland, Michigan 48640 (US)

(74) Representative:  
Patentanwälte  
Sternagel & Fleischer  
Braunsberger Feld 29  
51429 Bergisch Gladbach (DE)

(54) **Curable polyolefin compositions containing organosilicon compounds as adhesion additives**

(57) The adhesion of cured polyolefin compositions to a variety of substrates is improved using as the adhesion promoter the combination of 1) an organic or organosilicon compound containing at least one epoxy group and 2) at least one compound containing a) at least one silanol or carbinol group or a hydrolyzable silanol group precursor, and b) at least one group that reacts during curing of the polyolefin.

EP 0 984 034 A2

## Description

[0001] This invention provides curable polyolefin compositions that contain a specified group of adhesion promoting additives to achieve strong bonding to a variety of substrates, particularly glass and metals.

[0002] The properties of polyolefin compositions are desirable for a variety of end use applications, particularly in construction, packaging, automotive and consumer markets. The compositions are useful as pressure sensitive adhesives for paper labels, for sealing tires and as adhesives for assembly of single ply roofing. Recently there is a trend toward the use of curable polyolefin compositions. One benefit of these curable compositions is the ability to prepare solvent-less compositions which following application and curing exhibit properties similar to those of solvent-based adhesives.

[0003] A shortcoming of polyolefin compositions, particularly those that cure by a platinum group metal catalyzed hydrosilation reaction, is their inability to develop strong adhesion to a variety of substrates, particularly glass and certain metals, following curing under commercially feasible conditions of time and temperature. One method for remedying this deficiency is by using primer compositions or adhesion promoting additives containing one or more silanes and/or organosiloxanes with a plurality of silicon-bonded hydrolyzable groups and at least one organofunctional substituent that is bonded to silicon through at least one carbon atom.

[0004] Primer compositions are applied to substrates to which adhesion is desired prior to application of a curable composition. Adhesion promoters are present as additional ingredients in curable composition.

[0005] U.S. Patent 5,397,648 describes pressure sensitive compositions for automotive masking tape. The compositions include a moisture curable alpha olefin copolymer containing hydrolyzable or condensable silyl groups.

[0006] U.S. Patent 4,981,728 describes a method for bonding curable organic polymer compositions to a surface using a primer. The curable composition contains 1) an organic polymer with SiX units where X is OH or hydrolyzable group, 2) an epoxy resin, 3) a curing agent for the epoxy resin and 4) a curing agent for the organic polymer. The primer is a vinyl polymer containing Si bonded to OH or hydrolyzable group and is a reaction product of a) a vinyl-containing polymer, preferably a poly(meth)acrylate, and b) a silane or siloxane containing hydrogen and hydrolyzable groups bonded to silicon.

[0007] The use of organic or inorganic compounds containing epoxy groups as adhesion promoters for curable organosiloxane compositions is taught in the following prior art: U.S. Patents 5,232,959; 4,912,188 and 4,906,686.

[0008] Silanes containing silicon-bonded alkenyl or alkenyloxy groups in combination with an epoxy group are described in U.S. Patent 4,732,932;

[0009] The combination of a) a polyorganosiloxane containing SiOH and alkenyl groups and b) a silane containing epoxy and silicon-bonded alkoxy groups is described in U.S. Patent 4,087,585; and

[0010] U.S. Patent 5,595,826 teaches using the combination of 1) a compound containing at least one epoxy group and 2) a compound containing at least one hydroxyl group and at least one substituent selected from silicon-bonded hydrogen, alkenyl, acryl and methacryl.

[0011] Japanese Patent Application 9-316293 discloses curable compositions comprising 1) a hydrocarbon polymer containing in each molecule at least one ethylenically unsaturated group capable of participating in an hydrosilation reaction; 2) a curing agent containing at least two silicon-bonded hydrogen atoms per molecule; 3) a catalyst for promoting a hydrosilation reaction; 4) a compound referred to as a "silane coupling agent" and 5) an organoaluminum or organotitanium compound. The silane coupling agent is defined as a silane containing at least one alkoxy group and at least one organofunctional group selected from epoxy, methacrylyl, acrylyl, isocyanate, isocyanurate, vinyl and carbamate.

[0012] Our invention improves the adhesion of cured polyolefin compositions to a variety of substrates, using as the adhesion promoter the combination of 1) an organic or organosilicon compound containing at least one epoxy group; and 2) at least one compound containing a) a silanol or carbinol group and b) a group that reacts with substituents on the polyolefin during curing of the polyolefin.

[0013] The use of this class of adhesion promoters for organosiloxane compositions is described in the aforementioned U.S. Patent 5,595,826; however, there is no teaching of the utility of these compositions for improving the adhesion of compositions containing at least one curable polyolefin in place of organopolysiloxanes described in the patent.

[0014] The adhesion-promoting additives of this invention can be used with polyolefin compositions that cure using any of the following reactions:

- 1) the platinum group metal-catalyzed reactions of silicon-bonded hydrogen atoms with alkenyl radicals present on the polyolefin;
- 2) the reaction of ethylenically unsaturated substituents on the polyolefin with mercapto groups in the presence of a catalyst that is typically a metal carboxylate of a chelated organometallic compound such as ferrocene;
- 3) reactions involving the ethylenically unsaturated substituents present on the polyolefin with either free radicals or cations formed by irradiation of photosensitive compounds with ultraviolet light, and
- 4) reactions involving the ethylenically unsaturated substituents present on the polyolefin that are initiated by high

energy particles such as those present in electron beams.

[0015] This invention provides curable, self-adhering polyolefin compositions comprising

5 A. a polyolefin wherein each molecule contains at least two ethylenically unsaturated substituents capable of reacting to cure said polyolefin; and

B. an adhesion promoter for said polyolefin; wherein the adhesion promoter comprises

10 1) at least one compound B1 containing at least one epoxide group, wherein said compound B1 is selected from organic compounds or organosilicon compounds; and

2) at least one compound B2 containing a) at least one substituent selected from silanol (=SiOH), hydrolyzable silanol precursors or carbinol (=COH) and b) at least one substituent capable of reacting during curing of said polyolefin;

15 and wherein all compounds corresponding to compound B1 constitute from 10 to 90 percent of the combined weight of all compounds corresponding to compounds B1 and B2.

[0016] As used in this specification, the term "cure" means conversion of a liquid or semi-solid composition to a crosslinked gel, elastomer or resinous material by the reaction of ethylenically unsaturated substituents present on the polyolefin referred to as ingredient A of the present compositions with a curing agent.

20 [0017] The preferred curing reaction for the polyolefin is 1) the reaction of the alkenyl radicals, such as allyl, present on the polyolefin with 2) an organohydrogensiloxane. The curable composition preferably includes a platinum group metal or a compound of one of these metals as a catalyst for this curing reaction.

25 [0018] The characterizing feature of the present curable polyolefin compositions is the presence as an adhesion promoting additive of a mixture comprising 1) at least one organic or organosilicon compound containing at least one epoxide group, referred to herein as compound B1; and 2) at least one compound referred to herein as compound B2 and containing a) at least one silanol group, hydrolyzable silanol group precursor or carbinol group, and b) at least one substituent capable of participating in the reaction that occurs during curing of the polyolefin. Silicon-bonded alkoxy groups are examples of hydrolyzable silanol group precursors.

30 [0019] The total weight of all compounds corresponding to compound B1 constitutes from 10 to 90 percent, preferably from 33 to 80 percent, of the total weight of all compounds corresponding to compounds B1 and B2.

[0020] When compound B1 is an organic compound, it can contain from 3 to 100 carbon atoms.

35 [0021] Examples of organic epoxide compounds suitable for use as compound B1 include aliphatic epoxides such as propylene oxide and butylene oxide; cycloaliphatic epoxides such as cyclohexene oxide; the mono- and diglycidyl ethers of mono- and polyhydric alcohols such as hexanol, ethylene glycol and trimethylolpropane; the glycidyl ethers of phenols and the mono- and diglycidyl ethers of bis-phenols. Oligomers of epoxide compounds containing unreacted epoxy groups can also be used.

40 [0022] Examples of organosilicon compounds containing epoxide groups include silanes containing at least one epoxy group per molecule and organopolysiloxanes containing epoxy groups as a part of terminal and/or non-terminal repeating units of the molecule.

[0023] In addition to the epoxy group(s), the silanes useful as compound B1 contain at least one hydrolyzable group per molecule. Examples of hydrolyzable groups include alkoxy and acyloxy containing from 1 to 10 or more carbon atoms, isoalkoxy, ketoximo and aminoxy. These hydrolyzable groups should not interfere with curing of the polyolefin.

[0024] Preferred hydrolyzable groups are methoxy, ethoxy, isopropenoxy and acetoxy.

45 [0025] Compound B1 can optionally contain at least one functional group capable of reacting during curing of the curable polyolefin, referred to hereinafter as ingredient A, of the present curable compositions.

[0026] To facilitate blending with the other ingredients of the present curable compositions, the melting point of compound B1 is preferably below 70°C.

50 [0027] Preferred embodiments of compound B1 are 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, monomeric and oligomeric glycidyl ethers of bis-phenols such as bisphenol A and other organic epoxides such as propylene oxide and cyclohexene oxide. Other preferred embodiments of compound B1 are described in U.S. Patents 4,082,726, 4,087,585 and 5,595,826.

[0028] The second required ingredient of the adhesion-promoting additives of this invention, referred to herein as compound B2, contains 1) at least one hydroxyl group, silanol group or hydrolyzable silanol precursor and 2) at least one group capable of participating in the reaction used to cure the polyolefin into which the present adhesion promoters are incorporated. In preferred curable polyolefin compositions, this group contains ethylenic unsaturation.

[0029] When compound B2 is an alcohol, it is represented by the formula  $R^1(OH)_m$ .  $R^1$  in this formula is an ethylenically unsaturated hydrocarbon radical exhibiting a valence of m and containing at least 3 carbon atoms and m is an integer.

ger with a value of at least 1. The value of  $m$  is preferably from 1 to 3.

[0030] The hydrocarbon radical represented by  $R^1$  contains from 4 to 20 carbon atoms. Other than the presence of at least one ethylenically unsaturated group capable of participating in the curing reaction of the polyolefin (ingredient A), the structure of  $R^1$  is not limited. This radical includes linear, branched and/or cyclic hydrocarbon structures.  $R^1$  most preferably contains from 5 to 10 carbon atoms and is bonded to from 1 to 3 hydroxyl groups.

[0031] When compound B2 is a mono- or polyhydric alcohol, preferred embodiments include 1-undecenyl alcohol, 4-pentene-1-ol and dihydrocarveol.

[0032] When compound B2 contains silanol ( $\text{SiOH}$ ) groups or hydrolyzable silanol precursors such as alkoxy groups, these groups can be present in a silane corresponding to the general formula  $R^2_n R^3_p \text{SiY}_{(4-n-p)}$  or as part of a siloxane containing at least one siloxane unit with an  $\text{SiOH}$  group and at least one siloxane unit containing either a silicon-bonded alkenyl radical or a hydrocarbon radical containing an ethylenically unsaturated group such as acryloxy as a substituent. A silicon-bonded alkoxy group or other hydrolyzable group can be present in place of the silicon-bonded hydroxyl group.

[0033] In the foregoing formulae for the silane embodiment of compound B2,  $R^2$  represents a monovalent ethylenically unsaturated radical;  $R^3$  represents a monovalent hydrocarbon radical free of ethylenic unsaturation,  $n$  is from 1 to 3, inclusive,  $p$  is 0, 1 or 2 and  $Y$  is  $\text{OH}$  or a hydrolyzable group as a precursor for silanol functionality: with the proviso that the sum of  $n + p$  does not exceed 3.

[0034] The monovalent ethylenically unsaturated radical represented by  $R^2$  can be an alkenyl radical such as allyl, vinyl or the isomeric butenyl radicals. Alternatively,  $R^2$  can contain additional functional groups such as carboxyl and carboalkoxy. Embodiments of  $R^2$  containing ethylenically unsaturated functional groups include 3-methacryloxypropyl and 3-acryloxypropyl.  $R^2$  can contain from 2 to 20 or more carbon atoms.

[0035] The monovalent hydrocarbon radical represented by  $R^3$  contains from 1 to 20 or more carbon atoms and is free of substituents capable of participating in the reaction responsible for curing of the polyolefin.  $R^3$  can be a linear or branched alkyl radical such as methyl, ethyl and isopropyl; a cycloalkyl radical such as cyclohexyl; or an aromatic radical such as phenyl, tolyl or benzyl.  $R^3$  can contain substituents such as halogen atoms so long as these substituents do not participate in or interfere with curing of the polyolefin composition containing the present adhesion promoting additives.

[0036] When compound B2 is an organosiloxane, examples of preferred embodiments include liquid silanol-terminated organosiloxane homopolymers and copolymers containing at least one  $R^2 R^3 \text{SiO}$  unit. Most preferably,  $R^2$  is vinyl and  $R^3$  is methyl or ethyl. The term "liquid" implies that the compounds flow at 25°C.

[0037] In addition to compounds B1 and B2, the adhesion promoting additive referred to as ingredient B can include a catalytically effective amount of a catalyst for the reaction of the epoxide groups present in compound B1 with the hydroxyl or silanol groups present in compound B2. Suitable catalysts include chelated compounds of aluminum such as aluminum acetylacetone and zinc compounds such as zinc acetylacetone.

[0038] To improve the performance of the present adhesion promoting additives when cured coatings containing these additives are exposed to humid conditions, these additives can optionally include from 10 to 90 weight percent, preferably from 50 to 90 weight percent, based on the total weight of this additive, of at least one silane containing at least one silicon-bonded alkoxy or isoalkenyloxy group.

[0039] The optional silane, referred to hereinafter as compound B3, is represented by the general formula  $R^4_t \text{SiX}_{(4-t)}$ , where  $R^4$  represents a monovalent hydrocarbon radical,  $X$  represents an alkoxy or isoalkenyloxy group and  $t$  is 0 or an integer from 1 to 3, inclusive.

[0040] The hydrocarbon radical represented by  $R^4$  can contain from 1 to 10 or more carbon atoms and can be saturated or ethylenically unsaturated.

[0041]  $R^4$  is preferably an alkyl radical containing from 1 to 4 carbon atoms or an alkenyl radical containing from 2 to 15 carbon atoms and  $X$  is preferably an alkoxy radical containing from 1 to 4 carbon atoms.

[0042] Preferred silanes for optional compound B3 include tetramethoxysilane, tetraethoxysilane, methyltrimethoxysilane, methyltriethoxysilane and hexenyltrimethoxysilane.

[0043] When the adhesion promoting additive contains organosilicon compounds with silicon-bonded alkoxy or other groups that react to form siloxane bonds in the presence of moisture, the additive preferably includes a catalyst for this reaction. Suitable catalysts include organotitanium compounds such as tetrabutyl titanate.

[0044] The concentration of the present adhesion promoting additive, comprising the combination of compounds B1 and B2 together with the aforementioned optional compound B3 and catalysts, is sufficient to provide cohesive bonding of the cured polyolefin composition to the desired substrate. This typically requires at least 1 weight percent by weight of the adhesion promoting additive, based on the weight of the curable composition. A concentration of between 1.5 and 7.5 weight percent is preferred.

[0045] The ability of the polyolefin composition to cure completely under the desired conditions and/or the properties of the cured composition can be adversely affected when the total concentration of adhesion promoting additives exceeds 10 weight percent, based on the total weight of the curable composition.

[0046] For purposes of the present invention, acceptable cohesive bonding is characterized by cohesive failure, which occurs when the strength of the bond between the cured polyolefin and the substrate exceeds the tensile strength of the cured material.

[0047] During a typical adhesion determination, the substrate is immobilized while increasing force is applied along the interface between the substrate and the layer of cured material until at least a portion of the cured material separates from the substrate. Separation along the interface between the cured material and substrate is defined as adhesive failure. A separation within the layer of cured material is referred to as cohesive failure.

[0048] The ingredients of preferred curable polyolefin compositions suitable for use with the present adhesion promoting additives will now be discussed in detail.

10 [0049] The polyolefin, referred to hereinafter as ingredient A of the present curable compositions is the principal ingredient of these compositions. The polyolefin composition can cure to form a crosslinked product by a variety of reactions described hereinbefore involving the ethylenically unsaturated groups on this polymer.

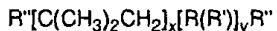
[0050] A preferred reaction for curing the polyolefin is a hydrosilation reaction between ethylenically unsaturated groups and silicon-bonded hydrogen atoms. This reaction requires the presence of a catalyst, which is a platinum group 15 metal or a compound thereof. Polyolefins curable by a hydrosilation reaction preferably contain at least two alkenyl or other ethylenically unsaturated radicals in each molecule. Suitable alkenyl radicals contain from 2 to 10 carbon atoms and are exemplified by vinyl, allyl and 5-hexenyl.

20 [0051] The molecular structure and molecular weight of the polyolefin are not critical to the present invention and will be determined by the physical properties desired in the cured composition. To achieve a useful level of tensile properties in the elastomers and other products prepared by curing the present compositions, the molecular weight of this ingredient should be sufficient to achieve a viscosity at 25°C. greater than 0.1 Pa · s.

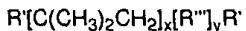
[0052] The upper limit for the molecular weight of the polyolefin is not specifically restricted and is typically limited only by the processability of the curable composition. The viscosity of the polyolefin can range from a pourable liquid to a gum type polymer that is typically characterized by Williams plasticity values.

25 [0053] The selection of monomer(s) used to prepare the polyolefin is not critical. One or more ethylenically unsaturated hydrocarbons containing from 2 to 10 carbon atoms can be used to prepare the polyolefin. Suitable hydrocarbons include but are not limited to ethylene, propylene, the isomeric butylenes, dienes such as butadiene and ethylenically unsaturated aromatic hydrocarbons such as styrene.

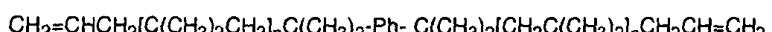
30 [0054] Preferred embodiments of ingredient A are isobutylene homopolymers and copolymers of isobutylene represented by the following general formulae I, II and III.



I.



II.



III.

35 [0055] In these formulae, R represents a trivalent hydrocarbon radical, R' and R'' are monovalent hydrocarbon radicals containing the  $-CH=CH_2$  group; R''' represents a divalent olefinically unsaturated hydrocarbon radical and Ph represents a phenyl radical. The degree of polymerization represented by n and the sum of x and y is equivalent to a viscosity at 25°C of at least 100 centipoise (0.1 Pa · s), preferably from 0.1 to 1000 Pa · s.

40 [0056] Preferred curable polyolefin compositions of our invention contain at least one organosilicon compound with at least two silicon-bonded hydrogen atoms that functions as a curing agent for the polyolefin, referred to as ingredient A. In the presence of the hydrosilation catalyst the silicon-bonded hydrogen atoms in the curing agent undergo a 45 hydrosilation addition reaction with the alkenyl groups in the polyolefin, resulting in crosslinking and curing of the composition.

[0057] Specific classes of preferred curing agents include silanes containing at least two silicon-bonded hydrogen atoms per molecule and organosiloxanes containing from 2 to 30 siloxane units and at least two silicon-bonded hydrogen atoms.

50 [0058] When the curing agent is an organohydrogensiloxane it can contain groups other than silicon-bonded hydrogen atoms, providing these additional groups do not interfere with curing of the polyolefin.

[0059] If the polyolefin contains only two alkenyl radicals per molecule, the curing agent must contain an average of more than two silicon-bonded hydrogen atoms to achieve a crosslinked structure in the final cured product.

55 [0060] The organic groups in the organohydrogensiloxane are preferably substantially free of ethylenic or acetylenic unsaturation. The molecular structure of the organohydrogen-siloxane can be straight chain, branch-containing straight chain, cyclic or network.

[0061] While the molecular weight of the preferred organohydrogensiloxane is not specifically restricted, viscosities in the range of 3 to 10,000 centipoise (0.003 to 10 Pa · s) at 25°C. are preferred.

[0062] The concentration of organohydrogensiloxane is sufficient to provide a molar ratio of silicon-bonded hydrogen atoms to alkenyl radicals in the curable composition of from 0.4 to 20. A range of from 0.4 to 4 is preferred.

[0063] When the curable composition contains less than 0.4 moles of silicon-bonded hydrogen atoms per mole of alkenyl radicals it may not be possible to achieve the desired physical properties following curing. The physical properties of the cured article may vary with time when this ratio exceeds about 20 moles of silicon-bonded hydrogen per mole of alkenyl radicals.

[0064] The reaction between silicon-bonded hydrogen atoms and ethylenically unsaturated groups is catalyzed by metals from the platinum group of the periodic table and compounds of these metals. These catalysts are present in compositions cured using this type of reaction. Platinum group metals include platinum, palladium and rhodium. Platinum compounds are preferred based on the high activity level of these catalysts in hydrosilation reactions.

[0065] Examples of preferred curing catalysts include platinum black, platinum metal on various solid supports, chloroplatinic acid, alcohol solutions of chloroplatinic acid and complexes of chloroplatinic acid with liquid ethylenically unsaturated compounds such as olefins and organosiloxanes containing ethylenically unsaturated hydrocarbon radicals bonded to silicon. Complexes of chloroplatinic acid with the aforementioned organosiloxanes containing ethylenically unsaturated hydrocarbon radicals are described in U.S. Patent 3,419,593.

[0066] The concentration of hydrosilation catalyst in the present compositions is equivalent to a platinum concentration of from 0.1 to 500 parts by weight of platinum metal, preferably from 1 to 50 parts by weight of platinum metal, per million parts (ppm), based on the combined weight of ingredients A and B.

[0067] Curing does not proceed satisfactorily at below 0.1 ppm of platinum, while using more than 500 ppm results in no appreciable increase in cure rate and is therefore uneconomical.

[0068] Mixtures of the aforementioned ingredients A, B and the hydrosilation catalyst may begin to cure at ambient temperature. To obtain a longer working time or "pot life", the activity of the catalyst under ambient conditions can be retarded or suppressed by addition of a suitable inhibitor.

[0069] Known platinum catalyst inhibitors include the acetylenic compounds disclosed in U.S. Patent 3,445,420. Acetylenic alcohols such as 2-methyl-3-butyn-2-ol constitute a preferred class of inhibitors that will suppress the activity of a platinum-containing catalyst at 25°C. Compositions containing these catalyst inhibitors typically require heating at temperatures of 70°C. or above to cure at a practical rate.

[0070] Alkenyl substituted siloxanes of the type described in U.S. Patent 3,989,667 increase the pot life of a curable composition under ambient conditions. Cyclic methylvinylsiloxanes are preferred.

[0071] Inhibitor concentrations as low as one mole of inhibitor per mole of platinum will in some instances impart satisfactory storage stability and cure rate. In other instances, inhibitor concentrations of up to 500 or more moles of inhibitor per mole of platinum are required. The type and concentration of inhibitor that will provide excellent adhesion in a given composition can readily be determined by routine experimentation and does not constitute part of this invention. Certain types of catalyst inhibitors may adversely affect the degree of adhesion that is developed under a given set of curing conditions relative to compositions containing a different type of catalyst inhibitor.

[0072] The present polyolefin compositions can contain one or more additives that are conventionally present in curable compositions of this type to impart or enhance desired physical properties other than adhesion to the cured composition or to facilitate processing of the curable composition.

[0073] Typical additives include processing aids, reinforcing fillers such as finely divided silica; non-reinforcing fillers such as quartz, alumina, mica and calcium carbonate; pigments such as carbon black and titanium dioxide; dyes, flame retardants and heat and/or ultraviolet light stabilizers.

[0074] The compositions of this invention can be prepared by combining all desired ingredients at ambient temperature. Any of the mixing techniques and devices described in the prior art can be used for this purpose. The particular device used will be determined by the viscosity of the ingredients and the final curable composition. Suitable mixers include paddle type mixers, kneader type mixers and two- or three-roll rubber mills.

[0075] Cooling of the ingredients during mixing may be desirable to avoid premature curing of the composition.

[0076] To maximize storage stability of polyolefin compositions that cure by a hydrosilation reaction, the curable compositions are preferably kept in closed containers until used. If greater storage stability is desired, the ingredients of the compositions can be packaged in two or more containers with the organohydrogensiloxane curing agent and the platinum group metal catalyst in separate containers.

[0077] Cured polyolefin materials prepared using the present compositions can vary in properties from brittle resins to elastomers to gels and are useful in a variety of end-use applications such as coatings or as molded or extruded articles.

[0078] Unfilled materials are particularly useful as gels and coatings for protecting delicate electronic devices such as integrated circuits from damage by moisture and other materials present in the environment that can adversely affect operation of the device. The compositions can be used to coat either the individual devices or a circuit board containing a number of these devices together with other electronic components.

[0079] Compositions containing reinforcing and/or non-reinforcing fillers are useful as adhesives, encapsulants and

potting materials.

[0080] The present compositions can be applied to substrates by spraying, dipping, pouring, extrusion or by the use of a brush, roller or coating bar. The selection of a particular application method will be determined at least in part by the viscosity of the curable composition. The viscosity of the composition can be reduced using suitable solvents.

[0081] The following examples describe preferred curable compositions of the present invention. Unless otherwise specified, all parts and percentages in the example are by weight and viscosities were measured at 25°C.

Example 1

[0082] This example demonstrates the excellent adhesion of a cured polyisobutylene composition to a variety of substrates that can be achieved using a preferred adhesion-promoting additive of the present invention.

[0083] Curable polyisobutylene compositions were prepared by blending the following ingredients to homogeneity:

92.96 parts of a filled polymer composition containing the following ingredients:

100 parts of a telechelic allyl -terminated polyiso-butylene exhibiting a molecular weight of 10,000 and containing 0.513 weight percent of allyl radicals;

100 parts of a liquid hydrogenated polybutene exhibiting an average molecular weight of 363 and available as Pannalane(R) L-14-E from Amoco Corporation;

100 parts of a precipitated calcium carbonate exhibiting an average particle size of 0.075 micrometer a surface area of 21 m<sup>2</sup> per gram and a stearate ester coating, and

50 parts of a ground calcium carbonate available from Georgia Marble as CS-11;

1.74 parts of a copolymer exhibiting the average molecular formula  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_3(\text{MeHSiO})_5\text{SiMe}_3$ , as the curing agent for the polymer;

5.2 parts of a mixture containing 0.4 parts of a complex of platinic chloride with sym-tetramethyldivinyldi-siloxane and 99.6 parts of the liquid hydrogenated polybutene referred to hereinbefore as Pannalane(R) L-14-E as the curing catalyst; (The complex contained 21 weight percent platinum.)

0.138 parts of cyclic methylvinylsiloxanes as the curing catalyst inhibitor;

0.5 part of 3-glycidoxypropyltrimethoxysilane as compound B1 of the present adhesion promoting additives;

0.5 part of a hydroxyl -terminated siloxane oligomer containing an average of 4 dimethylsiloxane and 1 methylvinyl-siloxane unit per molecule as compound B2 of the present adhesion promoting additive;

0.25 parts of hexenyltrimethoxysilane and 3.5 parts of tetraethyl ortho-silicate as optional adhesion promoters referred to hereinbefore as compound B3;

0.25 part of a 4 weight percent solution of aluminum acetylacetone in toluene as the catalyst for reaction of the epoxy groups present in the adhesion promoting additive; and

0.1 part of tetrabutyl titanate as the catalyst for hydrolysis of the silicon-bonded alkoxy groups in the composition.

[0084] Portions of each of the curable compositions evaluated were applied as 10 mil (0.25 mm)-thick liquid films to the desired substrate using a draw-down bar.

[0085] The liquid coatings on one group of substrates were cured under ambient conditions for 24 hours, 3 days or 7 days prior to evaluation.

[0086] The coatings on a second group of substrates were cured by heating at 70°C. for 30 minutes. A third group of coatings were cured at 120°C. for 90 minutes. The adhesion of one group of cured coatings was evaluated immediately following cooling. Additional groups of coated substrates were evaluated for adhesion after the substrates had remained under ambient conditions for 24 hours, 3 days and 7 days following heating. The coatings cured at 70°C. were also evaluated following storage for 14 days under ambient conditions.

[0087] Another set of liquid coatings were cured at 70°C. for 30 minutes following which the coated substrates were immersed in water for 24 hours, 3 days, 7 days or 14 days prior to being evaluated.

[0088] The substrates evaluated were glass and stainless steel (SS).

[0089] The adhesion test consisted of attempting to separate the cured coating from the substrate by inserting the blade of a metal spatula at the interface between the coating and the substrate and determining whether any of the coating could be separated from the substrate without leaving a liquid or solid residue from the coating on the surface of the substrate. The adhesion was rated 0 if the coating could be removed completely without leaving any solid residue. If some solid residue remained, the residue was rubbed using a fingertip to determine the pressure required to remove it and the adhesion was rated according to the following scale.

55 1 = light pressure required

2 = moderate pressure required

3 = heavy pressure required

EP 0 984 034 A2

4 = no coating could be removed under any pressure

[0090] The results of the evaluation are summarized in the following tables.

5

10

Room Temperature Cure			
Substrate	Adhesion Ratings		
	24 Hours	3 Days	7 Days
Glass	0	4	2
SS	4	4	4

15

20

25

70°C. Cure For 30 Minutes					
Substrate	Adhesion Ratings				
	Immediate	24 Hours	3 Days	7 Days	14 Days
Glass	4	4	4	4	4
SS	4	4	4	4	4

30

35

40

70°C. Cure For 30 Minutes Followed by 60°C. Water Immersion				
Substrate	Adhesion Ratings Following X Hours Immersion			
	X=24 Hrs	X=3 Days	X=7 Days	X=14 Days
Glass	4	4	4	4
SS	4	4	4	4

[0091] All of the coatings that were cured at 70°C. exhibited cohesive failure (a rating of 4) that was not adversely affected by immersion in water.

[0092] When cured at room temperature, cohesive failure was developed to steel after 24 hours and to glass after 3 days.

Example 2

[0093] This example demonstrates the improvement in adhesion achieved using the two ingredients of the present adhesion promoting additives relative to using either ingredient individually.

[0094] Curable polyisobutylene compositions were prepared by blending the following ingredients to homogeneity:

100 parts of the isobutylene polymer described in Example 1;  
A copolymer exhibiting the average molecular formula  $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_3(\text{MeHSiO})_5\text{SiMe}_3$  in the amounts specified in Table 3 in the column headed "SiH";

100 parts of parts of a liquid polyisobutylene exhibiting a number average molecular weight of 363;

100 parts of a calcium carbonate available as SPM Winnofil;

50 parts of a ground calcium carbonate available from Georgia Marble as CS-11;

4 0.14 part of cyclic methylvinylsiloxanes as a curing catalyst inhibitor;  
 5 0.1 part of tetrabutyl titanate;  
 5 0 or 0.25 part of aluminum acetylacetone (Al(acac)), a known catalyst for the reaction of epoxide compounds, as  
 a 4% by weight solution in toluene; and  
 5 30 ppm of platinum in the form of a complex of platinic chloride and sym-dimethylvinyl-disiloxane.

[0095] The following five adhesion additives of the present invention were evaluated:

10 as a compound B1; 3-glycidoxypropyltrimethoxy-silane (ingredient 1);  
 10 as a compound B2; a hydroxyl -terminated siloxane oligomer containing an average of 4 dimethyl-siloxane and 1  
 methylvinylsiloxane unit per molecule (ingredient 2);  
 15 as a compound B2, 1-undecylenyl alcohol (ingredient 3);  
 15 as a compound B2, the diallyl ether of trimethylolpropane (ingredient 4); and  
 15 as an optional silane (compound B3), tetraethyl orthosilicate (ingredient 5).

15 [0096] The number and amount of ingredients present in the compositions evaluated are summarized in the following  
 Table 3. Compositions 1 and 2 are outside the scope of the present invention and were evaluated for comparative pur-  
 poses.

20

Table 3

Composition No.	Ingredients (parts by weight)						
	1	2	3	4	5	Al(acac)	SiH
1 (C)	-	-	-	-	4.5	0	1.444
2 (C)	4.5	-	-	-	-	0	1.44
3	0.5	0.5	-	-	3.5	0.25	1.709
4	0.5	0.5	-	-	3.5	0	1.704
5	0.5	0.1	-	-	3.5	0	1.49
6	0.5	-	0.1	-	3.5	-	1.516
7	0.5	-	-	1.5	3.5	0	1.835
8	0.5	0.1	-	-	3.5	0.25	1.541
9	0.5	-	0.1	-	3.5	0.25	1.567

C = Comparative Composition

40

[0097] The curable compositions were evaluated by applying them as liquid films to substrates using the procedure described in the preceding Example 1 and then curing the films. The substrates evaluated were glass, bare aluminum (bare Al), milled aluminum (milled Al) and stainless steel (SS).

45

[0098] The liquid films were cured using the following temperature schedules: Under ambient conditions for 24 hours, 3 days and 7 days. At 70°C. for 30 minutes followed by an adhesion evaluation upon cooling and after remaining under ambient conditions for 24 hours, 3 days and 7 days. At 120°C. for 90 minutes followed by an adhesion evaluation upon cooling and after remaining under ambient conditions for 24 hours, 3 days and 7 days.

[0099] The results of the evaluations are summarized in Table 4. A rating of "NC" indicates that the composition did not cure under the specified conditions. The notation "NE" indicates that ambient temperature curing was not used.

50

55

Table 4

5	Sample	Room Temp.				700C			1200C			
		24 Hr.	3d	7d	Im.	24 Hr	3d	7d	Im	24 Hr	3d	7d
No. 1(C)												
10	Glass	NC	4	2	1	4	4	4	4	4	4	4
	Bare Al	NC	4	4	0	1	1	0	4	4	4	4
	Milled Al	NC	4	4	1	1	4	4	4	4	4	4
	SS	NC	4	4	0	2	1	2	0	2	1	2
No. 2(C)												
15	Glass	0	0	0	1	1	1	1	4	4	4	4
	Bare Al	0	0	0	0	0	0	0	1	0/4 <sup>1</sup>	0/4 <sup>1</sup>	0/4 <sup>1</sup>
	Milled Al	4	4	4	1	1	4	4	4	4	4	4
	SS	4	4	4	1	4	4	4	4	4	4	4
No. 3												
20	Glass	NC	0/4 <sup>1</sup>	0/4 <sup>1</sup>	4	4	4	4	4	4	4	4
	Bare Al	NC	0/4 <sup>1</sup>	0/4 <sup>1</sup>	4	4	4	4	4	4	4	4
	Milled Al	NC	0/4 <sup>1</sup>	0/4 <sup>1</sup>	4	4	4	4	4	4	4	4
	SS	NC	0/4 <sup>1</sup>	0/4 <sup>1</sup>	4	4	4	4	4	4	4	4
No. 4												
25	Glass	NC	PC	0/4 <sup>1</sup>	0/4 <sup>1</sup>	0/4 <sup>1</sup>	0/4 <sup>1</sup>	2	4	4	4	4
	Bare Al	NC	PC	0/4 <sup>1</sup>	4	4	4	4	4	4	4	4
	Milled Al	NC	PC	0/4 <sup>1</sup>	4	4	4	4	4	4	4	4
	SS	NC	PC	0/4 <sup>1</sup>	4	4	4	4	4	4	4	4
40												
45												
50												
55												

Table 4 (cont.)

5	Sample	Room Temp.				70°C			120°C			
		24 Hr.	3d	7d	Im.	24 Hr.	3d	7d	Im.	24 Hr.	3d	7d
No. 5												
10	Glass	0	0	0/4 <sup>1</sup>	4	4	4	4	4	4	4	4
Bare Al	0	4	4	1	4	4	4	0	0/4 <sup>1</sup>	0/4 <sup>1</sup>	4	
Milled Al	4	4	4	4	4	4	4	4	4	4	4	
SS	4	4	4	4	4	4	4	4	4	4	4	
No. 6												
15	Glass	1	1	0/4 <sup>1</sup>	4	4	4	4	4	4	4	
Bare Al	4	4	4	1	1	3	4	4	4	4	4	
Milled Al	4	4	4	4	4	4	4	4	4	4	4	
SS	4	4	4	4	4	4	4	4	4	4	4	
No. 7												
20	Glass	4	4	1	2	1	1	1	4	4	4	
Bare Al	4	4	4	1	1	1	1	4	4	4	4	
Milled Al	4	4	4	4	4	4	4	4	4	4	4	
SS	4	4	4	4	4	4	4	4	4	4	4	
No. 8												
25	Glass	NE	NE	NE	4	4	4	4	4	4	4	
Bare Al	NE	NE	NE	0	1	1	1	4	4	4	4	
Milled Al	NE	NE	NE	3	4	4	4	4	4	4	4	
SS	NE	NE	NE	1	4	4	4	4	4	4	4	
No. 9												
30	Glass	NE	NE	NE	4	4	4	4	4	4	4	
Bare Al	NE	NE	NE	0	1	1	4	4	4	4	4	
Milled Al	NE	NE	NE	1	4	4	4	4	4	4	4	
SS	NE	NE	NE	4	4	4	4	4	4	4	4	

NC= coating not cured

NE= curing condition not evaluated

1 = Rating of 0/4 indicates that degree of curing varied over surface of substrate.

Cured portions exhibited cohesive failure, partially cured portions did not.

55 [0100] For the coatings cured at room temperature, after 24 hours the composition containing prior art adhesion promoter 3-glycidoxypropyltrimethoxysilane adhered to milled aluminum and steel. Under the same curing conditions, compositions 6 and 7 of the present invention adhered to these substrates in addition to unfinished aluminum.

[0101] After 3 days at room temperature, prior art composition 1 and composition 7 of the present invention adhered to all substrates. Compositions 5 and 6 adhered to both types of aluminum and steel.

[0102] After 7 days, prior art composition 1 and compositions 5, 6 and 7 of the present invention adhered to both types of aluminum and steel.

5 [0103] Curing at 70 degrees substantially improved the performance of compositions 3-6 relative to curing under ambient conditions, but had an adverse effect on prior art composition 1 and resulted in only a minor improvement or a decrease in the adhesion of prior art composition 2. The adhesion of composition 7 of the present invention to glass and bare aluminum was adversely affected by the increase in curing temperature. Storage under ambient conditions resulted in cohesive failure of compositions 8 and 9 to three of the four substrates.

10 [0104] Almost all of the compositions tested exhibited cohesive failure when cured at 120°C. for 90 minutes.

[0105] Summarizing, the adhesion-promoting compositions of our invention developed excellent adhesion, evidenced by cohesive failure, under milder curing conditions than the single-ingredient adhesion promoters of the prior art containing the same types of reactive groups as the present compositions.

15 **Claims**

1. A self-adhering polyolefin composition comprising

20 A. a polyolefin wherein each molecule contains at least two ethylenically unsaturated substituents capable of reacting to cure said polyolefin; and

B. an adhesion promoter for said polyolefin; wherein the adhesion promoter comprises

25 (B1) at least one compound containing at least one epoxide group, wherein said compound B1 is selected from organic compounds or organosilicon compounds; and

25 (B2) at least one compound containing a) at least one substituent selected from silanol (=SiOH), hydrolyzable silanol precursors or carbinol (=COH) and (b) at least one substituent capable of reacting during curing of said polyolefin;

30 and wherein all compounds corresponding to compound B1 constitute from 10 to 90 percent of the combined weight of all compounds corresponding to compounds B1 and B2.

30 2. A composition according to claim 1 wherein compound B1 is selected from aliphatic epoxides; cycloaliphatic epoxides; the mono- and diglycidyl ethers of mono-and polyhydric alcohols, the glycidyl ethers of phenols, the mono- and diglycidyl ethers of bis-phenols, silanes containing at least one epoxy group per molecule or organopolysiloxanes containing at least one epoxy group per molecule; compound B2 is selected from (a) mono-hydric hydrocarbon alcohols, (b) polyhydric hydrocarbon alcohols, wherein the hydrocarbon portion of said alcohols is ethylenically unsaturated, and (c) silanes or (d) organopolysiloxanes, wherein said silanes and organopolysiloxanes contain (i) at least one substituent selected from silanol (SiOH) or hydrolyzable silanol precursors and (ii) at least one ethylenically unsaturated group per molecule; and wherein the weight of all compounds corresponding to compound B1 constitute from 33 to 80 percent of the combined weight of all compounds corresponding to compounds B1 and B2.

35 3. A composition according to claim 1 wherein compound B2 is an alcohol represented by the formula  $R^1(OH)_m$  wherein  $R^1$  represents an ethylenically unsaturated hydrocarbon radical exhibiting a valence of  $m$  and containing at least 3 carbon atoms and  $m$  is an integer with a value of at least 1.

40 4. A composition according to claim 1 wherein compound B2 is at least one member selected from the isomeric undecylenic alcohols, 4-pentene-1-ol or dihydrocarveol.

45 5. A composition according to claim 2 wherein compound B2 is selected from silanes exhibiting the general formula  $R^2_nR^3_pSiY_{(4-n-p)}$  or organopolysiloxanes containing in each molecule at least one substituent represented by Y and at least one siloxane unit wherein the silicon atom is bonded to an alkenyl radical or a hydrocarbon radical containing an ethylenically unsaturated substituent, wherein  $R^2$  represents a monovalent ethylenically unsaturated radical;  $R^3$  represents a monovalent hydrocarbon radical free of ethylenic unsaturation,  $n$  is from 1 to 3 inclusive,  $p$  is 0, 1 or 2; and Y represents OH or a hydrolyzable group, with the proviso that the sum of  $n + p$  does not exceed 3.

55 6. A composition according to any of the preceding claims where said adhesion promoter additionally comprises at least one of a compound B3 selected from silanes of the general formula  $R^4_1SiX_{(4-1)}$ , wherein  $R^4$  is selected from the group consisting of monovalent saturated and ethylenically unsaturated hydrocarbon radicals, X represents an

alkoxy or isoalkenyloxy group and t is 0 or an integer from 1 to 3, inclusive, and the combined weight of all compounds corresponding to compound B3 constitutes from 10 to 90 percent of the total weight of said additive.

7. A composition according to claim 6 wherein compound B1 is glycidoxypropyltrimethoxysilane; compound B2 is a hydroxyl-terminated organosiloxane oligomer wherein the repeating units are dimethylsiloxane and methylvinylsiloxane; and compound B3 is at least one member of the group consisting of hexenyltrimethoxysilane and tetraethyl orthosilicate.
8. A composition according to any of the preceding claims wherein the adhesion promoter B) is present in an amount of 1.0 to 10.0 weight percent preferably 1.5 to 7.5 weight percent based on the total weight of the composition.
9. A composition according to any of the preceding claims wherein said polyolefin is selected from the group consisting of homopolymers and copolymers of isobutylene and is flowable at 25°C.
10. A composition according to any of the preceding claims wherein said composition further comprises an organohydrogensiloxane curing agent for said polyolefin and a catalytically effective amount of a curing catalyst selected from the platinum group metals of the periodic table and compounds of said metals.

20

25

30

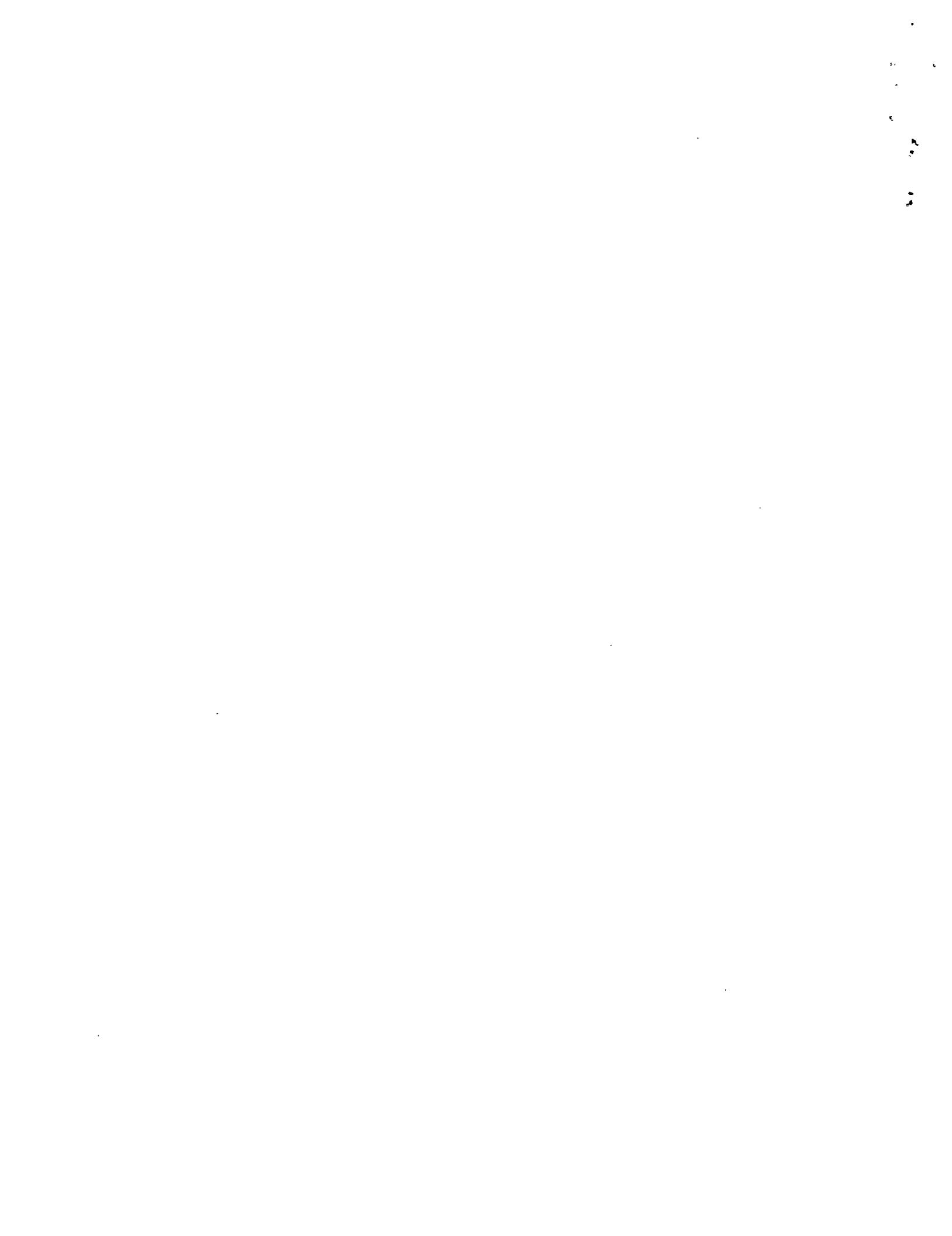
35

40

45

50

55



(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 0 984 034 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
22.03.2000 Bulletin 2000/12

(51) Int. Cl.<sup>7</sup>: C08K 5/5419, C09J 11/06,  
C09J 151/06, C09J 123/26

(43) Date of publication A2:  
08.03.2000 Bulletin 2000/10

(21) Application number: 99116148.0

(22) Date of filing: 19.08.1999

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE

Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 04.09.1998 US 148805

(71) Applicant:  
DOW CORNING CORPORATION  
Midland, Michigan 48686-0994 (US)

(72) Inventors:  
• Feng, Qian Jane  
Midland, Michigan 48640 (US)

• Lee, Kenneth Michael  
Bay City, Michigan 48708 (US)  
• Lutz, Michael Andrew  
Hope, Michigan 48628 (US)  
• Owen, Michael James  
Midland, Michigan 48640 (US)  
• Perz, Susan Victoria  
Essexville, Michigan 48632 (US)  
• Suzuki, Toshio  
Midland, Michigan 48640 (US)

(74) Representative:  
Patentanwälte  
Sternagel & Fleischer  
Braunsberger Feld 29  
51429 Bergisch Gladbach (DE)

(54) Curable polyolefin compositions containing organosilicon compounds as adhesion additives

(57) The adhesion of cured polyolefin compositions to a variety of substrates is improved using as the adhesion promoter the combination of 1) an organic or organosilicon compound containing at least one epoxy group and 2) at least one compound containing a) at least one silanol or carbinol group or a hydrolyzable silanol group precursor, and b) at least one group that reacts during curing of the polyolefin.

EP 0 984 034 A3



European Patent  
Office

## EUROPEAN SEARCH REPORT

**Application Number**

EP 99 11 6148

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	EP 0 850 996 A (DOW CORNING) 1 July 1998 (1998-07-01) * page 2, line 19 - page 4, line 40 * * page 6, line 21 - line 37 * * examples 1,2 * ----	1-10	C08K5/5419 C09J11/06 C09J151/06 C09J123/26
D,Y	US 5 595 826 A (GRAY THOMAS E ET AL) 21 January 1997 (1997-01-21) * column 2, line 23 - line 43 * * column 4, line 16 - column 6, line 23 * * column 9, line 5 - line 14; examples 8-12; table 2 * ----	1-10	
			<p>TECHNICAL FIELDS SEARCHED (Int.Cl.7)</p> <p>C08L C08G C08K C09J</p>
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	26 January 2000	Parry, J	
CATEGORY OF CITED DOCUMENTS			
X	particularly relevant if taken alone	T theory or principle underlying the invention	
Y	particularly relevant if combined with another document of the same category	E earlier patent document, but published on or after the filing date	
A	technological background	D document cited in the application	
O	non-written disclosure	L document cited for other reasons	
P	intermediate document	.....	
		B member of the same patent family, corresponding document	

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 99 11 6148

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The member's are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-01-2000

Patent document Cited in search report		Publication date		Patent family member(s)		Publication date
EP 0850996	A	01-07-1998		US 5928794 A		27-07-1999
				AU 4854097 A		25-06-1998
				JP 10330628 A		15-12-1999
US 5595826	A	21-01-1997		DE 69600968 D		17-12-1998
				DE 69600968 T		15-07-1999
				EP 0768342 A		16-04-1997
				JP 9111125 A		28-04-1997

EPO FORM PA/169

For more details about this annex see Official Journal of the European Patent Office, No. 12/82

